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(21) International Application Number: PCT/US83/01871 (22) International Filing Date: 30 November 1983 (30.11.83) (71) Applicant (for JP only): E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventor; and (75) Inventor/Applicant (for US only) : JOHNSON, Bruce, Bjorge, [US/US]; 315 Palmers Lane, Wallingford, PA 19086 (US). (74) Agent: HASEK, William, R.; Legal Department, E.I. du Pont de Nemours and Company, 1007 Market Street, Wilmington, DE 19898 (US). (81) Designated States: JP, US.		Published <i>With international search report.</i>
(54) Title: ZERO GAP CELL (57) Abstract A zero-gap membrane electrolytic cell using a membrane with a bubble release layer on each side is used with a coarse mesh porous electrode on one side and a fine mesh porous electrode with a current distributor on the other side.		

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TITLE

ZERO GAP CELL

BACKGROUND

Membrane cells using fluorinated cation
5 exchange membranes have been used for electrolysis,
particularly for the electrolysis of aqueous alkali
metal chloride solutions to make chlorine and
alkaline metal hydroxides. If a suitable membrane
with bubble release surfaces is used, the cell
10 voltage can be reduced by using a zero gap cell, in
which both electrodes are urged against but not
bonded to the membrane. These cells have been of
complex and expensive construction, in which both
electrodes may be of expensive fine metal mesh,
15 backed with a current distributor (Japanese laid-open
patent application J57/41387 to Asahi Glass) or the
cathode may be backed with a resilient compressible
material (U.S. 4,340,542 to Oronzio de Nora) or may
use grooved anodes (U.S. 4,057,479 to Billings) or
20 corrugated anodes (U.S. 4,056,452 to Billings) or
tangled fibrous electrodes (Japanese laid-open patent
application J57/134579 to Showa Denko).

SUMMARY OF THE INVENTION

In the present invention a rugged, simple,
25 relatively inexpensive cell construction is used.
One electrode, preferably the anode, comprises a
coarse porous conductor having less than 20
openings/cm² and at least 50% open area, the
conductor being selected from expanded metal,
30 flattened expanded metal, woven wire screen, and
perforated plate. The other electrode comprises a
fine mesh, e.g. a fine expanded metal mesh or a fine
wire screen, having more than 20 openings/cm² and
at least 50% open area, supported by a coarser and
35 more rigid current distributor having less than 20



openings/cm². The electrodes are urged against the membrane by any suitable method, but are not bonded to it and may be disassembled when one component needs to be replaced.

5

DETAILED DESCRIPTION OF THE INVENTION

The anode for a chlor-alkali cell should be electrically conductive material resistant to corrosion by brine and chlorine, resistant to erosion, and preferably may contain an electrocatalyst to minimize chlorine overvoltage. The well-known dimensionally stable anode is among those that are suitable. A suitable base metal is titanium, and the electrocatalysts include reduced platinum group metal oxides (such as Ru, etc.) singly or in mixtures, optionally admixed with a reduced oxide of Ti, Ta, Cb, Zr, Hf, V, Pt, or Ir.

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It may be desirable to have the anode openings slanted so the gas is carried away from the membrane and anolyte circulation past the membrane is maximized. This effect can be augmented by using downcomers for anolyte which has been lifted by the rising gas bubbles.

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An anodic electrocatalyst preferably comprises reduced oxides of ruthenium or such oxides in combination with at least one reduced oxide from the group consisting of the reduced oxides of iridium, tantalum, titanium, niobium, and hafnium, preferably iridium. More preferably a combination of 75 to 95% by wt., most preferably 75% by wt., of reduced oxides of ruthenium, and 25 to 5% by wt., most preferably 25% by wt., of reduced oxides of iridium is used. It is best to thermally stabilize the reduced oxides of ruthenium by heating, to produce a composition which is stable against chlorine and oxygen evolution. Such electrocatalyst

and its stabilization by heating are described in U.S. Patents 4,224,121 and 3,134,697, and UK Patent Application GB 2 009 788A.

5 Both the anode and the cathode must be porous so they are permeable to liquid electrolytes and gaseous products. The open area must be at least 40%, preferably at least 50%.

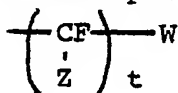
10 The cathode for a chloralkali cell should be electrically conductive material resistant to corrosion by the catholyte, resistant to erosion, and preferably may contain an electrocatalyst to minimize hydrogen overvoltage. The cathode may be mild steel, nickel, or stainless steel, for example, and the electrocatalyst may be platinum black, palladium,
15 gold, spinels, manganese, cobalt, nickel, Raney nickel, reduced platinum group metal oxides, or alpha-iron.

20 It is desirable that the electrode have open vertical channels or grooves to facilitate the evolution of the cathode gas, which is hydrogen in many cell processes. It may be desirable to have the cathode openings slanted so the gas is carried away from the membrane and catholyte flow past the membrane is maximized. This effect may be augmented
25 by using downcomers for catholyte which has been lifted by rising gas bubbles.

One electrode comprises a coarse conductor preferably coated with electrocatalyst, as described above, with less than 20 openings/cm², preferably
30 less than 15 openings/cm². The other electrode comprises a fine mesh, preferably coated with electrocatalyst, the mesh having more than 20 openings/cm². It is supported by a relatively coarse, non-resilient current collector having less
35 than 20 openings/cm². The current collector which

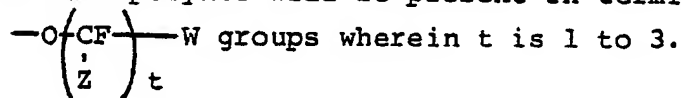
contacts the cathode may be made of any metal which is a good conductor and is resistant to corrosion by the electrolyte, preferably nickel. The current collector which contacts the anode may be made of any metal which is a good conductor and is resistant to corrosion by the electrolyte, preferably titanium coated to enhance its surface conductivity.

The carboxylic polymers with which the present invention is concerned have a fluorinated hydrocarbon backbone chain to which are attached the functional groups or pendant side chains which in turn carry the functional groups. When the polymer is in melt-fabricable form, the pendant side chains can contain, for example,



groups wherein Z is F or CF_3 , t is 1 to 12, and W is $-\text{COOR}$ or $-\text{CN}$, wherein R is lower alkyl.

Preferably, the functional group in the side chains of the polymer will be present in terminal



By "fluorinated" is meant a membrane in which, after loss of any R group by hydrolysis to ion exchange form, the number of F atoms is at least 90% of the total number of F, H and Cl atoms in the polymer. For chloralkali cells, perfluorinated membranes are preferred, though the R in any COOR group need not be fluorinated because it is lost during hydrolysis.

Polymers containing $-(\text{OCF}_2\text{CF})_m\text{OCF}_2\text{CFCN}$ side chains, in which m is 0, 1, 2, 3 or 4, are disclosed in U.S. 3,852,326.

Polymers containing $-(CF_2)_p COOR$ side chains, where p is 1 to 18, are disclosed in U.S. 3,506,635.

Polymers containing $-(OCF_2CF)_m OCF_2 COOR$ side chains, where Z and R have the meaning defined above and m is 0, 1, or 2 (preferably 1) are disclosed in U.S. 4,267,364.

Polymers containing terminal $-O(CF_2)_v W$ groups, where W is as defined above and v is from 2 to 12, are preferred. They are disclosed in U.S. 3,641,104, U.S. 4,178,218, U.S. 4,116,888, British 2,053,902A, EP 41737 and British 1,518,387. These groups may be part of $-(OCF_2CF)_m -O-(CF_2)_v -W$ side chains, where $Y = F$ or CF_3 or CF_2Cl . Especially preferred are polymers containing such side chains where v is 2, which are described in U.S. 4,138,426 and S. Afr. 78/002225, and where v is 3, which are described in U.S. 4,065,366. Among these polymers, those with $m=1$ and $Y=CF_3$ are most preferred.

The above references describe how to make these polymers.

The sulfonyl polymers with which the present invention is concerned are fluorinated polymers with side chains containing the group $-CF_2CF SO_2 X$, wherein R_f

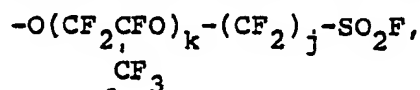
R_f is F , Cl , CF_2Cl or a C_1 to C_{10} perfluoro-alkyl radical, and X is F or Cl , preferably F .

Ordinarily, the side chains will contain

$-OCF_2CF_2CF_2SO_2X$ or $-OCF_2CF_2SO_2F$ groups, preferably the latter. The term "fluorinated" carries the same meaning as employed above in reference to carboxylate

membranes. For use in chloralkali synthesis, perfluorinated membranes are preferred.

Polymers containing the side chain



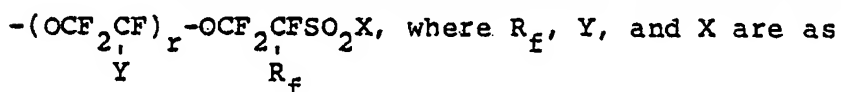
where k is 0 or 1 and j is 3, 4, or 5, may be used.

These are described in British 2,053,902A.

Polymers containing the side chain

$-\text{CF}_2\text{CF}_2\text{SO}_2\text{X}$ are described in U.S. 3,718,627.

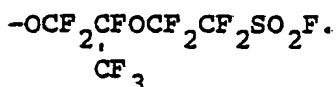
Preferred polymers contain the side chain



defined above and r is 1, 2, or 3, and these polymers

are described in U.S. 3,282,875. Especially

preferred are copolymers containing the side chain



Polymerization can be carried out by the methods described in the above references.

Especially useful is solution polymerization using $\text{ClF}_2\text{CCFCl}_2$ solvent and $(\text{CF}_3\text{CF}_2\text{COO})_2$ initiator.

Polymerization can also be carried out by aqueous granular polymerization as in U.S. 2,393,967, or

aqueous dispersion polymerization as in

U.S. 2,559,752 followed by coagulation as in U.S. 2,593,583.

The copolymers used in the layers described herein should be of high enough molecular weight to produce films which are self-supporting in both the melt-fabricable precursor form and in the hydrolyzed ion exchange form.

A membrane having at least one layer of a copolymer having sulfonyl groups in melt-fabricable form and a layer of a copolymer having carboxyl

groups in melt-fabricable form, such as made by coextrusion, can be used as one of the component films in making the membrane of the invention. Such a laminated structure may be referred to in this application as a bimembrane. Preparation of bimembranes is described in Japanese laid-open patent application J52/36589.

The customary way to specify the structural composition of films or membranes in this field of art is to specify the polymer composition, ion-exchange capacity or its reciprocal, equivalent weight, and thickness of the polymer films in melt-fabricable form, from which the membrane is fabricated. This is done because the measured thickness varies depending on whether the membrane is dry or swollen with water or an electrolyte, and even on the ionic species and ionic strength of the electrolyte, even though the amount of polymer remains constant.

For use in ion exchange applications and in cells, for example a chloralkali cell for electrolysis of brine, the membrane should have all of the functional groups converted to ionizable functional groups. These will be sulfonic acid and carboxylic acid groups, or preferably alkali metal salts thereof. When the term "sulfonic ion exchange groups" is used, it includes not only the sulfonic acid group but particularly the alkali metal salts thereof. Similarly, the term "carboxylic ion exchange groups" means the carboxylic acid group and particularly the alkali metal salts thereof. The alkali metals preferred for use in this invention are potassium and sodium, particularly sodium, which leads to the production of sodium hydroxide.

Conversion to ionizable functional groups is ordinarily and conveniently accomplished by hydrolysis with acid or base, such that the various functional groups described above in relation to the melt-fabricable polymers are converted respectively to the free acids or the alkali metal salts thereof. Such hydrolysis can be carried out with an aqueous solution of a mineral acid or an alkali metal hydroxide. Base hydrolysis is preferred as it is faster and more complete. Use of hot solutions, such as near the boiling point of the solution, is preferred for rapid hydrolysis. The time required for hydrolysis increases with the thickness of the structure. It is also of advantage to include a water-miscible organic compound such as dimethyl sulfoxide in the hydrolysis bath, to swell the membrane to increase the rate of hydrolysis.

Membranes usually have an overall thickness of 50-250 micrometers, especially 125-200 micrometers. The ion-exchange capacity of the carboxylate polymer is in the range of 0.7-1.4 meq/g, preferably 0.8-1.2 meq/g dry resin, with higher ion-exchange capacities providing more concentrated caustic during operation of a chlor-alkali cell at maximum current efficiency. The ion-exchange capacity of the sulfonate polymer is in the range of 0.5-1.5 meq/g, preferably 0.7-1.2 meq/g dry resin.

The membrane may be unreinforced, but for dimensional stability and greater notched tear resistance, it is common to use a reinforcing material. It is customary to use a fabric made of a fluorocarbon resin such as polytetrafluoroethylene or a copolymer of tetrafluoroethylene with hexafluoropropylene (Teflon® FEP fluorocarbon resin) or with perfluoro-(propyl vinyl ether) (Teflon® PFA

fluorocarbon resin). These may be woven into fabric using various weaves, such as the plain weave, basket weave, leno weave, or others. Relatively open weaves are favorable in that electrical resistance is lower. Porous sheet such as disclosed in US 3,962,153 may be used as a support. Other perhalogenated polymers such as polychlorotri-fluoroethylene may also be used, but perfluorinated supports have the best resistance to heat and chemicals. The fibers used in the support fabrics may be monofilaments or multifilament yarns. They may be of ordinary round cross-section or may have specialized cross-sections. Oblong or rectangular cross-sections, if suitably oriented to the membrane, make it possible to get more reinforcing action with a thinner overall membrane. It is desirable to use soluble or degradable fibers, such as rayon or paper, along with the fluorocarbon fibers, or in place of the fluorocarbon fibers. Care should be taken, however, not to have the soluble or degradable fibers extend from one surface to the other, or the non-porous membrane will become a porous diaphragm and, in the case of a chloralkali cell, the caustic will contain too much salt. Even with a cloth or mesh of fluorocarbon fibers, it is preferred not to have the cloth penetrate the surface of the membrane on the cathode side. The fabric employed may be calendered before lamination to reduce its thickness. In a bimembrane, the fabric may be in the sulfonate or carboxylate layer or both, but is more often in the sulfonate layer, which is usually thicker. In place of fabric, non-woven fibrils can be used.

The membrane or bimembrane may be used flat in various known filter press cells, or may be shaped



around an electrode. The latter is especially useful when it is desired to convert an existing diaphragm cell to a membrane cell in order to make better quality caustic.

5 New or used membranes may be swelled with polar solvents (such as lower alcohols or esters, tetrahydrofuran, or chloroform) and then dried, preferably between flat plates, to improve their electrolytic performance. Before mounting in
10 commercial cell support frames, which may be 1-3 meters on a side, the membrane may be swelled so that it will not wrinkle after it is clamped in the frame and exposed to electrolytic fluids. Among the swelling agents that can be used are water, brine,
15 caustic, lower alcohols, glycols, and mixtures thereof.

Bipolar or monopolar cells can be used. In ordinary use, the carboxylate side of the membrane will face the cathode. One can use (n) cells in
20 series, with anolyte flowing from cell (1) to cell (n) and catholyte flowing from cell (n) to cell (1). All these cells may use identical membranes, or different membranes may be used in different cells. Membranes using only polymers having pendant side
25 chains with terminal $-\text{CF}_2-\text{SO}_3^-$ groups may be used in cell (n) and possibly others near it. Cell (n) may be two or more cells in parallel.

The membrane may be disposed horizontally or vertically in the cell, or at any angle from the
30 vertical.

It has long been known that in the electrolysis of brine to make chlorine and caustic, it is desirable to use NaCl of low Ca and Mg content (Kobe, Inorganic Process Industries, Mac Millian,
35 1948, p 130; Rogers' Industrial Chemistry, Van



Nostrand, 1942, p 362). This is stated for electrolysis in general, for diaphragm electrolysis, for mercury electrolysis, and for membrane electrolysis (Water Pollution Control Research Series "Hypochlorite Generator for Treatment of Combined Sewer Overflows," 1972, US Environmental Protection Agency, pp 60-61). It was also well known how to remove hardness from sodium chloride solutions to very low levels. Heavy metals like iron and mercury and foreign anions like iodide should also be substantially removed. Some of the contaminants in make-up brine can be removed by passing the brine through a diaphragm cell before it is fed to the membrane cell system. Further hardness reductions can be achieved by passing the brine through a chelate ion exchanger, preferably one containing $\text{-NHCH}_2\text{COOH}$ groups, or a phosphate may be added to the brine to precipitate insoluble salts.

Brine fed to the cell is usually close to the saturation concentration, but lower brine concentration is acceptable. Brine leaving the anolyte chamber may be as low as about 2% by weight NaCl, but is more often 10-15 wt % NaCl, or even higher.

Because a bimembrane has lower electrical resistance than an all-carboxylate membrane, it can be operated at lower voltage or higher current density. Good results can be obtained at 10-70 A/dm^2 , preferably 30-50 A/dm^2 . Anolyte acidity is normally adjusted to a value in the range of pH 1-5 by addition of hydrochloric acid or hydrogen chloride to the recycle brine. Recycle brine may be concentrated by addition of solid salt and/or by evaporating or distilling water from the stream.

While membrane cells are frequently operated at approximately atmospheric pressure, there can be advantages to operating them at elevated pressure. While direct current is ordinarily used in membrane cells, one can also use pulsed direct current or half-wave AC or rectified AC or DC with a square wave.

Chlor-alkali synthesis is normally carried out at about 70-100°C. The catholyte can be kept 5-20° cooler than the anolyte temperature.

The membranes described herein should be modified on either surface or both surfaces so as to have enhanced gas release properties, for example by providing optimum surface roughness or smoothness by hot roll embossing or by embossing with a porous paper. When embossing with a porous paper, a release paper can be applied to an outer surface of the membrane while passing it through a laminator used, for example, to apply a reinforcement for the membrane. Such surface embossing is further described in U.S. Patent 4,349,422 to Maloney. Preferably the resulting surface roughness is about 2-5 microns as measured, for example, on a Bendix Model 1020 profilometer.

Preferably, the gas release properties of the membranes are enhanced by providing on at least one surface a gas- and liquid-permeable porous non-electrode layer, and if only one surface is coated, by roughening the other surface as described above. Such non-electrode layer can be in the form of a thin hydrophilic coating and is ordinarily of an inert electroinactive or non-electrocatalytic substance. Such non-electrode layer should have a porosity of 10 to 99%, preferably 30 to 70%, and an average pore diameter of 0.01 to 2000 microns, preferably 0.1 to 1000 microns, and a thickness

generally in the range of 0.1 to 500 microns, preferably 1 to 300 microns. A non-electrode layer ordinarily comprises an inorganic component and a binder; the inorganic component can be an inorganic compound which is chemically stable in hot concentrated caustic and chlorine, and can be of a type as set forth in published UK Patent Application GB 2,064,586A, preferably tin oxide, titanium oxide, zirconium oxide, or an iron oxide such as Fe_2O_3 or Fe_3O_4 . Other information regarding non-electrode layers on ion-exchange membranes is found in published European Patent Application 0,031,660, and in Japanese Laid-open Patent Applications 56-108888 and 56-112487. The particle size of the inorganic material can be about 1-100 microns, and preferably 1-10 microns. The weight loading for each coated side is 0.1-5%, preferably 0.5-1.0%, of the weight of the coated membrane.

The binder component in a non-electrode layer can be, for example, (a) polytetrafluoroethylene, (b) a fluorocarbon polymer at least the surface of which is hydrophilic by virtue of treatment with ionizing radiation in air or a modifying agent to introduce functional groups such as $-\text{COOH}$ or $-\text{SO}_3\text{H}$ (as described in published UK Patent Application GB 2,060,703A) or treatment with an agent such as sodium in liquid ammonia, (c) a functionally substituted fluorocarbon polymer or copolymer which has carboxylate or sulfonate functional groups, or (d) polytetrafluoroethylene particles modified on their surfaces with fluorinated copolymer having acid type functional groups (GB 2,064,586A). Such binder can be used in an amount of about from 10 to 50% by wt. of the non-electrode layer. In addition to the inorganic component and

the binder, the dispersion used to apply the inorganic component can include a thickener such as methyl cellulose or polyvinyl alcohol and a small amount of nonionic surfactant.

5 Composite structures having non-electrode layers thereon can be made by various techniques known in the art, which include preparation of a decal which is then pressed onto the membrane surface, spray application of a slurry in a liquid
10 composition (e.g., dispersion or solution) of the binder followed by drying, screen or gravure printing of compositions in paste form, hot pressing of powders distributed on the membrane surface, and other methods as set forth in British Patent
15 2,064,586A or Japanese Laid-open patent application J57/89490. Such structures can be made by applying the indicated layers onto membranes in melt-fabricable form, and by some of the methods onto membranes in ion-exchange form; the polymeric
20 component of the resulting structures when in melt-fabricable form can be hydrolyzed in known manner to the ion-exchange form.

The cell of the invention operates at lower voltage and lower power consumption when compared to
25 a similar cell having two coarse electrodes or to a similar cell having a narrow gap between the membrane and an electrode.

EXAMPLE 1

TFE/EVE refers to a copolymer of
30 tetrafluoroethylene and methyl perfluoro(4,7-dioxa-5-methyl-8-nonenoate).

TFE/PSEPVE refers to a copolymer of tetrafluoroethylene and perfluoro(3,6-dioxa-4-methyl-7-octenesulfonyl fluoride).
35



The following membrane structure was prepared by coextrusion.

A) A first layer consisting of a 102 micron (4 mil) layer of TFE/PSEPVE copolymer having an equivalent weight of 1100.

B) A second layer consisting of a 38 micron (1.5 mil) layer of TFE/EVE copolymer having an equivalent weight of 1050.

The anode surface of the membrane was roughened by embossing with a release paper.

The membrane was then hydrolyzed in an aqueous bath containing 30% dimethyl sulfoxide and 11% KOH for 20 minutes at 90°C. The cathode surface of this membrane was then coated with a dispersion of ZrO_2 and acid form TFE/PSEPVE having an equivalent weight of 950 in ethyl alcohol.

A membrane cell was assembled from the following components.

1) An expanded titanium anode coated with titanium oxide/ruthenium oxide. This anode had an open area of 60% and 2.2 openings per square centimeter.

2) A platinized 20 mesh nickel hardware cloth cathode which had an open area of 52% and 62 openings per square centimeter.

The cell was assembled with the membrane and cathode screen sandwiched between the anode and the cathodic current collector such that the anode and the membrane were in contact and both the membrane and the cathodic current collector were in contact with the cathode screen. The cell was operated at 90°C with an anolyte concentration of 220 gpl (grams per liter) NaCl at a current density of 3.1 kA/m^2 to make chlorine and caustic soda. Current efficiency was 96%, cell voltage was 3.06 Volts, and

the power consumption was 2129 kwh/metric ton of caustic.

COMPARATIVE EXAMPLE A

5 A membrane cell was assembled using the
membrane and the anode of Example 1. A platinized
solid nickel flattened expanded metal mesh with an
open area of 60% and 1.6 openings per square
centimeter was used for the cathode. The cell was
assembled with the membrane sandwiched between the
10 anode and the cathode such that both the anode and
the cathode were in contact with the membrane. The
cell was operated with an anolyte concentration of
about 220 gpl at a current density of 3.1 kA/m^2 to
make chlorine and caustic soda. Current efficiency
15 was 97%, cell voltage was 3.14 volts, and power
consumption was 2162 kwh/metric ton of caustic.

COMPARATIVE EXAMPLE B

The cell of Comparative Example A was then
taken apart and reassembled with a gap of 3mm between
20 the membrane and the platinized cathode. The
membrane was held against the anode by a hydraulic
head. The cell was operated at 90°C at a current
density of 3.1 kA/m^2 to make chlorine and caustic
soda. Current efficiency was 97%, cell voltage 3.25
25 volts, and power consumption was 2238 kwh/metric ton
of caustic.

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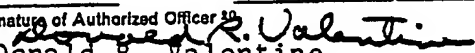


CLAIMS:

1. A zero-gap electrolytic cell, having a cathode chamber containing (a) a porous cathode made of conductive material having at least 50% open area, (b) a fluorinated cation exchange membrane with a bubble release layer on each surface, and an anode chamber containing (c) a porous anode made of conductive material having at least 50% open area, all three components (a), (b), and (c) being urged into intimate contact with the adjacent component but being capable of disassembly, characterized in that one electrode comprises a coarse conductor having less than 20 openings/cm², selected from expanded metal, flattened expanded metal, woven wire screen, and perforated plate, while the other electrode comprises a fine mesh having more than 20 openings/cm², supported with a coarser and more rigid current collector comprising a coarse conductor having less than 20 openings/cm².
2. The cell of Claim 1 in which the coarse electrode is the anode, both electrodes are coated with electrocatalysts, and the membrane is perfluorinated.
3. The cell of Claim 1 in which the membrane is coated prior to cell assembly with a porous non-electrode coating on one side and the other side has a roughness of 2 to 5 microns.
4. The cell of Claim 1 in which the membrane is coated on both sides prior to cell assembly with a porous non-electrode coating.
5. The cell of Claim 1, 2, 3, or 4 in which the coarse electrode has no more than 15 openings/cm² and the fine mesh electrode has no less than 50 openings/cm².

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US83/01871

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ¹		
According to International Patent Classification (IPC) or to both National Classification and IPC INT. CL3: C25B9/00; C25B 11/03; C25B 13/08 U.S. CL.: 204/252; 204/266; 204/283; 204/284; 204/290R; 204/296		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
U.S.	204/252, 266, 283, 284, 290R, 296	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁴		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category ¹⁵	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
Y	U.S. A, 4,417,959, 29 November 1983, (Kadija et al)	1-2
Y	U.S. A, 4,411,749, 25 October 1983, (Sato et al)	1-4
Y	U.S. A, 4,394,229, 19 July 1983, (Korach)	1, 5
Y	U.S. A, 4,389,297, 21 June 1983, (Korach)	1-2, 5
Y	U.S. A, 4,364,815, 21 December 1982 (Continued on Supplement Sheet 2)	1-2, 5
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁹ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ¹	Date of Mailing of this International Search Report ²	
24 February 1984	02 MAR 1984	
International Searching Authority ³	Signature of Authorized Officer ⁵	
United States	 Donald R. Valentine	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No ¹⁸
A	U.S. A, 4,360,416, 23 November 1982, (Davidson et al)	1, 2
A	U.S. A, 4,272,353, 09 June 1981 (Lawrance et al)	3
A	U.S. A, 4,323,434, 06 April 1982, (Yoshida et al)	3
A	U.S. A, 4,331,521, 25 May 1982, (Chisholm et al)	1-2